2005-01-2193

Regulated and Unregulated Exhaust Emissions Comparison for Three Tier II Non-Road Diesel Engines Operating on Ethanol-Diesel Blends

Patrick M. Merritt, Vlad Ulmet
Southwest Research Institute

Robert L. McCormick
National Renewable Energy Laboratory

William E. Mitchell
WM Consulting, Inc.

Kirby J. Baumgard
John Deere Power Systems

ABSTRACT

Regulated and unregulated emissions (individual hydrocarbons, ethanol, aldehydes and ketones, polynuclear aromatic hydrocarbons (PAH), nitro-PAH, and soluble organic fraction of particulate matter) were characterized in engines utilizing duplicate ISO 8178-C1 eight-mode tests and FTP smoke tests. Certification No. 2 diesel (400 ppm sulfur) and three ethanol/diesel blends, containing 7.7 percent, 10 percent, and 15 percent ethanol, respectively, were used. The three, Tier II, off-road engines were 6.8-L, 8.1-L, and 12.5-L in displacement and each had differing fuel injection system designs. It was found that smoke and particulate matter emissions decreased with increasing ethanol content. Changes to the emissions of carbon monoxide and oxides of nitrogen varied with engine design, with some increases and some decreases. As expected, increasing ethanol concentration led to higher emissions of acetaldehyde (increases ranging from 27 to 139 percent). Benzene emissions were reduced by up to 50 percent with the ethanol-blended fuels. Emissions of 1,3-butadiene were also substantially decreased, with reductions ranging from 24 to 82 percent. Isolated trends were noted for certain PAHs. There was a decrease in 1-nitropyrene with use of ethanol in all cases. Particulate phase 1-nitropyrene was reduced from 18 to 62 percent. There was also a general increase in the proportion of heavy PAHs in the particulate phase with ethanol use, and although less pronounced, a general decrease in light PAHs in the particulate phase.

INTRODUCTION

Blending of ethanol into diesel fuel may become an important petroleum displacement strategy, if certain technical barriers can be overcome: most importantly, the issues of low flashpoint and tank vapor flammability[1], as well as fuel stability during storage.[2] One source states that blending ethanol into gasoline currently reduces the need to import 128,000 barrels a day of oil into the USA.[3] Other issues, such as durability of engines operating on such fuels, are also important and must be considered. Investigations into lubricity and injector pump wear have been reported using bench test rigs,[4] but discussions of fuel injector and fuel system issues in actual on-engine applications have not been made. It is also important to understand the pollutant emission impacts of blending ethanol into diesel fuel. Prior emissions studies have focused mainly on regulated pollutant emissions while a limited number have included unregulated (mainly carbonyl compound) emissions; for further reading, a review was recently prepared by Corkwell, et. al.[5]

This project involved tests of Tier II compliant, non-road diesel engines to establish the overall impact of diesel-ethanol blends on regulated engine exhaust emissions, along with a number of unregulated toxic compounds. Four different fuel formulations were used in the engine performance and exhaust emissions evaluations. Three different models of off-road diesel engines were used to assess any effects from differing injection system types, or other mechanical differences. The engines were tested for gaseous emissions and smoke according to EPA Part 89 requirements. In addition to total hydrocarbons, oxides of nitrogen, carbon monoxide, carbon dioxide and

particulate matter, analyses were performed (on the 8-mode tests only) to quantify individual hydrocarbons, aldehydes, ketones, alcohols, polynuclear aromatic hydrocarbons (PAH), 1-nitropyrene, and soluble organic fraction (SOF) of particulate matter.

METHODS

TEST ENGINES

John Deere provided three heavy-duty, Tier II compliant, non-road diesel engines for this test program. These engines represent different fuel system and emissions control technologies and varied in displacement from 6.8 to 12.5 liters. The engine characteristics are summarized in Table 1 and include the three most common types of fuel injection systems.

TEST FUELS

The reference fuel for this program was No. 2D certification diesel, with a nominal sulfur content of 400 ppm. Three different blends of ethanol in this reference fuel were prepared, at 7.7, 10, and 15 percent by volume. Three additive suppliers provided material to enhance the stability and performance of the ethanol in diesel blends. The identity of the additive in a particular fuel blend is confidential, to prevent any use of the data for commercial advantage. For the sake of this program, they are simply designated as "A," "B," and "C." For each of the three ethanol concentrations, a separate blend was prepared utilizing one of each of the three additives. Thus, there resulted a matrix of nine candidate fuels, and one reference fuel. However, only one of each of the three additive blends for each ethanol concentration was run in each engine. Please see Table 2 for matrix of engines and fuels actually tested. The SwRI internal fuel codes

are also shown. Each of the three additives was run in one of the engines at each ethanol concentration.

Instructions provided by each additive manufacturer were followed for addition of additive during fuel blending. Additive concentrations (treat rates) varied from 1 to 2.57 percent by volume. Results of analyses of key properties of the ethanol and of the blended fuels are presented in Appendix A. To preclude absorption of water from the atmosphere during storage, a flow of nitrogen in the tank headspace was maintained.

EMISSIONS TEST PROCEDURES

Exhaust emission characterization was performed as specified under CFR Title 40, Part 89. For non-road heavy-duty engines, the regulation outlines specific requirements for setting up the test engine and pre-test activities, as well as all aspects of conducting the testing and collection and analysis of gaseous samples. The 8-mode test cycle was utilized in this test program. Table 3 shows the Part 89 test modes and weighting factors.

Two consecutive runs of the 8-mode test and two FTP smoke tests (40 CFR Parts 86 and 89) were performed for each fuel composition. In a regular 8-mode test we stabilize the engine for 5 minutes and sample for 5 minutes. To accumulate a sufficient dilute exhaust sample for unregulated emissions analysis, each mode was run for a number of minutes equivalent to its weight factor in percent (stabilization time of 5 minutes was unchanged). For example, a mode with a 0.10 weight factor received a ten-minute sampling period. This approach extended the total sampling duration for the 8-mode test from 40 to 100 minutes. For the PAH and NPAH sampling, one set of collection media was used to collect a composite sample for each 8-mode test.

TABLE 1. TEST ENGINE CHARACTERISTICS

Engine Model	6081HRW28	6068HF275	6125HRW02
Displacement, L	8.1	6.8	12.5
Rated Speed, rpm	2200	2000	2100
Rated Power, kW (hp)	224 (301)	129 (172)	375 (500)
Intermediate Speed, rpm	1400	1400	1500
Peak Torque, N-m (lb-ft)	1361 (1004)	725 (535)	1989 (1467)
Inlet Restriction, kPa (in. water)	2.99 (12)	2.99 (12)	2.99 (12)
Exhaust Restriction, kPa (in. mercury)	7.45 (2.2)	7.45 (2.2)	7.45 (2.2)
Turbocharged/Inter-cooled	Yes/Yes	Yes/Yes	Yes/Yes
Inter-cooling type	Air/Air	Air/Air	Air/Air
Inter-cooler Outlet Temperature, °C (°F)	60 (140)	60 (140)	60 (140)
Inter-cooler ΔP, kPa (in. water)	12.45 (50)	12.45 (50)	12.45 (50)
Fuel System	High pressure, common rail	Rotary pump line nozzle	Electronic unit injector

TABLE 2. TEST FUEL MATRIX

Engine ID	Additive	Cert. Fuel	7.7% Blend	10% Blend	15% Blend
John Deere 8.1-L	NONE	EM-4970-F			
	A		EM-4929-F		
	B			EM-4936-F	
	C				EM-4951-F
John Deere 6.8-L	NONE	EM-4970-F			
	A				EM-4949-F
	B		EM-4930-F		
	C			EM-4937-F	
John Deere 12.5-L	NONE	EM-4970-F			
	A			EM-4935-F	
	B				EM-4950-F
	C		EM-4932-F		

TABLE 3. PART 89 TEST MODES AND WEIGHTING FACTORS

Mode	1	2	3	4	5	6	7	8
Speed	Rated				Intermediate			Idle
Percent Torque	100	75	50	10	100	75	50	0
Weight Factor	0.15	0.15	0.15	0.10	0.10	0.10	0.10	0.15

EMISSIONS SAMPLING AND ANALYSIS PROCEDURES – REGULATED EMISSIONS

Regulated emissions determined on the 8-mode test included total hydrocarbon (HC), carbon monoxide (CO), oxides of nitrogen (NOx), carbon dioxide (CO2), and total particulate matter (PM). These emissions were collected and analyzed utilizing procedures that conform to the requirements stated in 40 CFR Part 89.

EMISSIONS SAMPLING AND ANALYSIS PROCEDURES – UNREGULATED EMISSIONS

The target list for unregulated emissions included the soluble organic fraction of the PM (SOF), aldehydes and ketones (ALD), ethanol (ETH), individual hydrocarbons (IHC), polycyclic aromatic hydrocarbons (PAH), and 1-nitropyrene. For each mode, SOF was determined by extracting a 50 percent section of the particulate-laden 90mm Pallflex filters using a Soxhlet apparatus with toluene-ethanol solvent. Solvent is evaporated from the extracted particulate filters and the filters are re-weighed. The difference in mass is the solvent-extractable material.

Individual hydrocarbons were measured from proportional bag samples of dilute exhaust for each mode using gas chromatography. Compounds ranging from C1 to C12, are identified and quantified in a process that requires four separate chromatographs. The process is based on the Auto/Oil Phase II Hydrocarbon Speciation procedure.[6] Full hydrocarbon speciation includes analysis of aldehydes, ketones, and alcohols if oxygenates are present in the fuel. Currently, EPA has identified four compounds that it has classified as

"toxic."[7] Those compounds are benzene, 1,3-butadiene, formaldehyde, and acetaldehyde.

Aldehydes and ketones (collectively known as carbonyl compounds) were sampled from the dilute exhaust for each mode utilizing impingers containing a solution of dinitrophenylhydrazine (DNPH) in acetonitrile. The highly reactive carbonyl compounds form stable derivatives with DNPH, which absorb ultra-violet light energy at specific wavelengths. These samples were analyzed using a high-pressure liquid chromatograph (HPLC) instrument using a ternary eluent gradient program (acetonitrile-water-methanol) with an ultraviolet detector.

Ethanol samples were collected for each mode utilizing impingers containing pure water. An aliquot was subsequently analyzed using gas chromatography with flame ionization detection (GC-FID).

The PAH and 1-nitropyrene are distributed in both the particulate and the gaseous phase of the dilute exhaust, and are difficult to measure at low concentrations. Additionally, there was concern that the sampling system has a "memory" for some PAH; therefore, additional effort to condition the sampling system with exhaust from the fuel under test was desirable. To accommodate these concerns, only after routing exhaust from several practice runs and preparatory operations through the constant volume sampler (CVS), was dilute engine exhaust sampling performed for record, using one composite sample for the entire 8-mode test. The composite sample approach increased the level of complexity of the sampling system but gave an almost eightfold analytical sensitivity and analysis cost benefit. During each five-

minute engine stabilization period at the beginning of each mode prior to emission sampling, the dilute exhaust sample flow going to the PAH samples was diverted, in order to protect the integrity of the 8-mode sample.

The dilute exhaust sampling process for PAH is described as follows. For the particulate-phase sampling, a single 20x20-inch Pallflex filter was used to collect particulate-phase PAH for the whole duration of each 8-mode test. Another filter was then used for the "blank" sampling, during which only the dilution tunnel was turned on (no engine operation). It was operated for the same duration as the entire 8-mode test.

Similarly, for the gas-phase PAH collection, a set of four PUF/XAD-2 traps was run in parallel over the full, 8-mode sequence to accumulate gas-phase PAH compounds. Four parallel traps were required to give sufficient gas flow (sample size) for meaningful detection limits. The PUF/XAD-2 trap set was extracted to generate a separate sample for the gas-phase PAH analysis.

Only the samples from one of each duplicate, 8-mode test (particulate- and gas-phase) were processed for final analysis of the PAH emissions. The samples from the second 8-mode test were extracted and stored as a backup. Subsequent to each 8-mode test, a "blank" sample, using a period of time similar to that used to accumulate dilute exhaust samples, was taken.

Following sample cleanup and derivativization, the extracts were analyzed by gas chromatography / mass spectrometry (GC/MS). The GC/MS system used included an Agilent 6890N GC equipped with a G2613A Automatic Sampler and interfaced to an Agilent 5973N MS detector. Injections (1 μL) were made in the splitless mode onto a 60 m 5% phenylmethylsilicone fused-silica capillary column (DB-5ms, J&W Scientific). Analysis of the PAH compounds was performed by GC/MS in positive ion/electron impact/selective ion monitoring (PI/EI/SIM) mode. The molecular ion or characteristic ion of each compound of interest and deuterated PAH, added as internal standards prior to extraction, were monitored. The NPAH and deuterated NPAH (internal standards) were quantified using the same GC/MS described above. However, the GC/MS was operated in negative ion/chemical ionization/SIM (NI/CI/SIM) mode. This technique is proven to be much more sensitive for the N-PAH's than using PI/EI/SIM technique.

RESULTS

8.1-Liter Engine Results

A summary of averaged, composite values for the duplicate, 8-mode tests of the 8.1-L engine operating on each fuel are presented in Table 4 and in Figure 1. (Note that NO_x is divided by ten to use the same scale.)
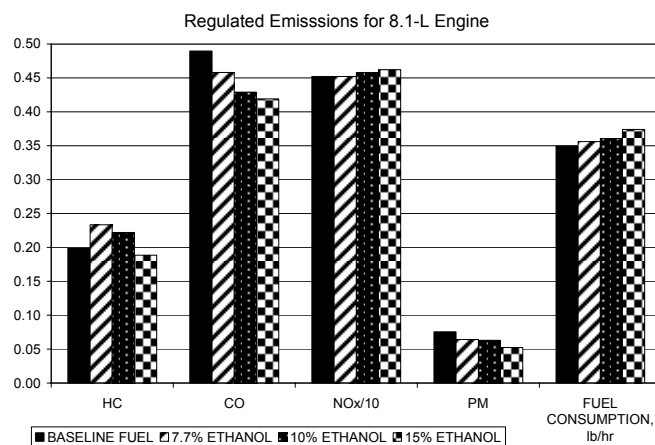

Figure 1. Regulated Emissions and Fuel Consumption for 8.1-L Engine

Carbon balance fuel consumption (C-B FC) is computed from the emissions data, while observed fuel consumption (OBS. FC) is derived from integrated measurement of flow and calculated work. Both are weighted average brake specific expressions. These values generally agree closely.

Emissions of hydrocarbons generally increased with the ethanol blends. The highest result, however, was observed with the 7.7 percent blend and dropped off with increasing ethanol content, to being slightly less than the baseline result for the 15 percent blend. Carbon monoxide and particulate emissions showed a definite reduction in line with increasing ethanol content. Emissions of NO_x increased slightly as ethanol content increased.

TABLE 4. REGULATED EMISSIONS SUMMARY FOR 8.1-LITER ENGINE
AVERAGED, COMPOSITE RESULTS OVER 8-MODE TEST

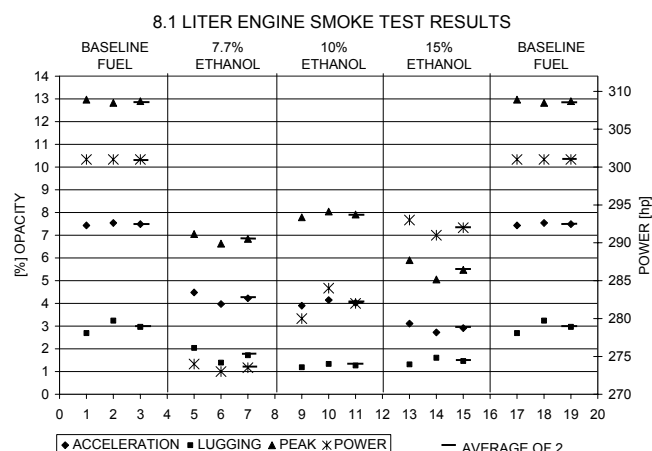| FUEL TYPE	BASELINE FUEL	7.7% ETHANOL	10% ETHANOL	15% ETHANOL	BASELINE FUEL
HC, g/bhp-hr	0.195	0.235	0.220	0.190	0.196
CO, g/bhp-hr	0.490	0.460	0.430	0.420	0.491
NO_x, g/bhp-hr	4.52	4.52	4.58	4.62	4.43
Particulate, g/bhp-hr	0.076	0.064	0.063	0.053	0.082
CO2, g/bhp-hr	503	497	501	503	501
C-B FC, lb/bhp-hr	0.35	0.36	0.36	0.37	0.35
OBS. FC, lb/bhp-hr	0.34	0.35	0.35	0.37	0.35

Figure 2. Smoke Test Results for 8.1-L Engine

Smoke test results are presented in Figure 2. Results indicated a reduction in opacity trending with increasing ethanol content under acceleration, lugging, and peak modes. This figure also captures the lower power levels measured with the different ethanol concentrations.

Soluble organic fraction of particulate matter is summarized in Table 5. SOF tended to increase with ethanol content as compared to baseline diesel fuel. SOF levels were, as expected, highest for the low load modes 4 and 8. Mode 7 exhibited the largest difference in SOF between baseline diesel fuel and an ethanol blend (in this case the 15% blend).

Individual hydrocarbon emissions results are summarized in Table 6. Increase emissions of formaldehyde, acetaldehyde, and ethanol were observed with increasing ethanol content. Emissions of 1,3-butadiene and benzene were reduced slightly with the ethanol blends.

PAH and NPAH results presented in Table 7. Please note that PAH and NPAH compounds are expressed in nanograms (10^{-9}g). In the vapor phase, acenaphthylene and fluorene are lower for the alcohol blends, but fluoranthene and pyrene are higher. An increasing trend with alcohol content is observable for benzo(a)anthracene and chrysene in this view. For the lighter molecular weight compounds in the particulate-phase, all compounds are lower in the ethanol blends than in the baseline diesel. For the heavier molecular weight compounds in the particulate-phase, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)-pyrene, indeno(1,2,3-cd)pyrene, and dibenzo(a,h)anthracene are all higher for the ethanol blends, but 1-nitro-pyrene is lower.

TABLE 5. SOLUBLE ORGANIC FRACTION BY MODE FOR 8.1-L-ENGINE PERCENT OF TOTAL PARTICULATE MATTER

Fuel Type	Baseline Average	7.7% Ethanol	10% Ethanol	15% Ethanol
Soluble Organic Fraction, percent of total particulate				
Mode 1	40.5	56.3	58.2	58.0
Mode 2	35.9	48.8	41.4	48.6
Mode 3	38.2	40.2	39.4	39.0
Mode 4	88.4	88.0	87.6	93.0
Mode 5	33.6	39.7	37.1	45.1
Mode 6	30.8	44.1	38.4	49.5
Mode 7	46.7	66.5	48.8	67.7
Mode 8	87.9	93.6	82.9	90.0

TABLE 6. UNREGULATED EMISSIONS SUMMARY FOR 8.1-LITER ENGINE AVERAGED, COMPOSITE RESULTS OVER 8-MODE TEST, mg/hp-hr

FUEL TYPE	BASELINE FUEL	7.7% ETHANOL	10% ETHANOL	15% ETHANOL
FORMALDEHYDE	9.56	10.21	10.52	11.00
ACETALDEHYDE	3.70	4.71	4.68	5.51
ACROLEIN	1.87	1.83	1.43	1.59
PROPIONALDEHYDE	0.68	0.83	1.18	1.22
METHYL ETHYL KETONE	0.53	0.59	0.09	0.09
ETHANOL	0.32	16.58	17.65	26.89
1,3-BUTADIENE	0.90	0.92	0.68	0.68
METHANE	2.09	0.32	0.53	0.15
BENZENE	0.81	0.70	0.69	0.72
TOLUENE	1.00	1.61	0.90	1.17
ETHYLBENZENE	0.51	0.53	0.42	0.55
m-& p-XYLENE	0.85	0.74	0.61	0.89
o-XYLENE	0.39	0.34	0.38	0.43
HEXANE	0.03	0.11	0.07	0.16
STYRENE	0.12	0.07	0.11	0.10

TABLE 7. PAH and NPAH COMPOUNDS FOR 8.1-L ENGINE, COMPOSITE RESULTS OVER 8-MODE TEST, ng/hp-hr

FUEL TYPE	BASELINE FUEL		7.7 % ETHANOL		10 % ETHANOL		15 % ETHANOL	
COMPOUND/PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE
Naphthalene	224515	237	234480	84	472781	144	219800	95
Acenaphthylene	1244	146	271	72	277	97	49	62
Acenaphthene	30207	89	30172	51	35886	63	30678	41
Fluorene	59566	471	47348	207	56904	295	45485	162
Phenanthrene	99538	7419	91207	3428	103191	4084	76198	2244
Anthracene	6519	710	6443	331	6842	368	5123	208
Fluoranthene	2274	2390	2935	348	3266	1627	2657	919
Pyrene	3674	5146	6413	3741	6267	3959	5685	2493
Benzo(a)anthracene	7	358	16	428	13	403	17	275
Chrysene	16	834	30	830	30	877	35	617
Benzo(b)fluoranthene	2	145	1	179	2	183	1	160
Benzo(k)fluoranthene	2	84	1	155	1	126	0	125
Benzo(a)pyrene	1	87	0	171	1	136	0	111
Indeno(1,2,3-cd)pyrene	1	14	1	27	1	32	1	34
Dibenzo(a,h)anthracene	2	5	0	8	0	10	0	8
1-Nitropyrene	0	129	1	68	1	90	2	79

6.8-LITER ENGINE RESULTS

A summary of averaged, composite values for the duplicate, 8-mode tests of the 6.8-L engine operating on each fuel are presented in Table 8 and in Figure 3. For the 6.8-L engine, there was no observable trend for hydrocarbon emissions. Carbon monoxide emissions increased with increasing ethanol content, and particulate emissions showed the opposite trend. Emissions of oxides of nitrogen were reduced with the ethanol-blended fuels, but were relatively constant regardless of ethanol content.

Smoke test results are presented in Figure 4 and soluble organic fraction of particulate matter is summarized in Table 9. For the 6.8-L engine, smoke opacity was reduced in proportion to ethanol content for all operational modes. SOF was highest for modes 4 and 8 and in general was higher with increasing ethanol content. Results for modes 1 and 8 did not follow this trend, however, where SOF was reduced with the ethanol blended fuels.

Significant increases were observed in emissions of acetaldehyde (and of ethanol) with increasing ethanol content. Emissions of 1,3-butadiene were reduced with ethanol blends, but benzene emissions were not significantly affected. Individual hydrocarbon emissions results are summarized in Table 10.

PAH results presented in Table 11. For the lighter molecular weight compounds for the vapor phase only, phenanthrene is lower for the alcohol blends, but fluoranthene and pyrene are higher. For the lighter molecular weight compounds in the particulate phase only most compounds are lower in the ethanol blends. In the heavier molecular weight compounds for the particulate phase, all compounds except 1-nitropyrene are higher in the ethanol blends. Lower emission rates are seen for 1-nitropyrene with the ethanol blends.

TABLE 8. REGULATED EMISSIONS SUMMARY FOR 6.8-LITER ENGINE AVERAGED, COMPOSITE RESULTS OVER 8-MODE TEST

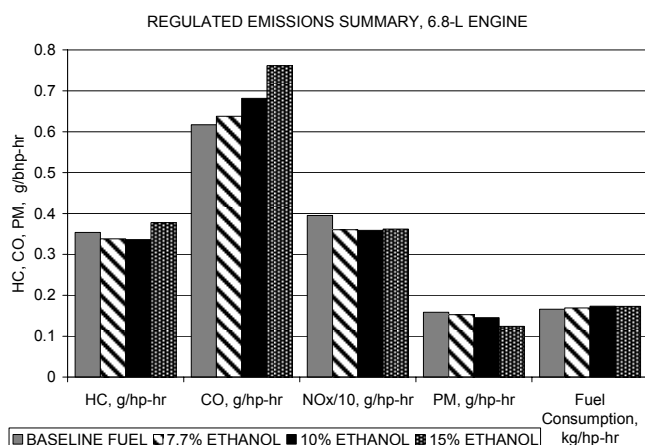| FUEL TYPE	BASELINE FUEL	7.7% ETHANOL	10% ETHANOL	15% ETHANOL	BASELINE FUEL
HC, g/bhp-hr	0.35	0.34	0.34	0.38	0.33
CO, g/bhp-hr	0.62	0.64	0.68	0.76	0.60
NO_x, g/bhp-hr	3.95	3.60	3.59	3.62	3.84
Particulate, g/bhp-hr	0.159	0.153	0.145	0.124	0.169
CO2, g/bhp-hr	526	518	526	522	516
C-B FC, lb/bhp-hr	0.37	0.37	0.38	0.38	0.38
OBS. FC, lb/bhp-hr	0.35	0.36	0.36	0.36	0.34

Figure 3. Regulated Emission Summary and Fuel Consumption for 6.8-L Engine
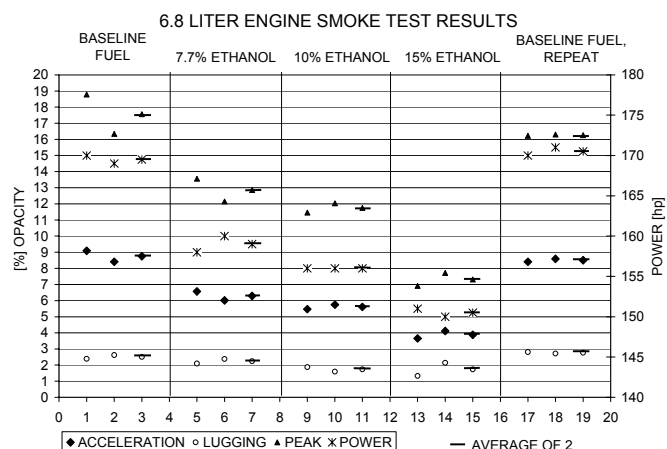

Figure 4. Smoke Test Results For 6.8-L Engine

TABLE 9. SOLUBLE ORGANIC FRACTION BY MODE FOR 6.8-L ENGINE, PERCENT OF TOTAL PARTICULATE MATTER

Fuel Type	BASELINE FUEL		7.7% ETHANOL		10% ETHANOL		15% ETHANOL	
Replicate	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
Mode 1	12.8	16.6	11.4	12.7	11.7	13.8	15.3	12.4
Mode 2	22.1	21.4	26.6	23.5	19.5	26.5	36.3	33.0
Mode 3	50.1	48.9	53.9	66.0	49.6	61.8	73.8	63.0
Mode 4	78.9	83.5	84.8	80.4	75.8	84.3	83.4	88.5
Mode 5	6.8	11.7	10.9	9.3	8.5	11.8	14.7	14.4
Mode 6	28.7	21.8	26.5	22.2	29.9	27.2	34.1	33.2
Mode 7	46.5	48.8	60.5	48.4	58.7	60.1	58.3	62.2
Mode 8	91.4	85.9	61.3	75.2	92.8	88.2	67.9	>99.0

TABLE 10. UNREGULATED EMISSIONS SUMMARY FOR 6.8-LITER ENGINE AVERAGED, COMPOSITE RESULTS OVER 8-MODE TEST, mg/hp-hr

COMPOUND/FUEL TYPE	BASELINE FUEL	7.7% ETHANOL	10% ETHANOL	15% ETHANOL
FORMALDEHYDE	16.56	14.77	14.88	20.11
ACETALDEHYDE	4.82	6.27	7.56	10.82
ACROLEIN	2.04	0.47	0.75	2.68
PROPIONALDEHYDE	2.35	1.32	1.39	1.81
METHYL ETHYL KETONE	0.15	0.13	0.30	0.16
ETHANOL	0.44	23.22	32.82	52.66
1,3-BUTADIENE	1.70	1.40	0.56	1.03
METHANE	0.71	1.14	2.37	3.11
BENZENE	1.78	1.68	1.79	1.82
TOLUENE	3.05	0.84	1.80	1.83
ETHYLBENZENE	0.90	0.68	0.51	0.76
m-& p-XYLENE	1.36	0.97	0.95	2.08
o-XYLENE	0.63	0.50	0.60	1.50
HEXANE	0.11	0.26	0.36	0.48
STYRENE	0.26	0.18	0.11	0.19

**TABLE 11. PAH and NPAH COMPOUNDS FOR 6.8-L ENGINE,
COMPOSITE RESULTS OVER 8-MODE TEST, ng/HP-HR**

FUEL TYPE	BASELINE FUEL		7.7% ETHANOL		10% ETHANOL		15% ETHANOL	
COMPOUND/PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE
Naphthalene	390119	408	108331	371	245566	299	381781	161
Acenaphthylene	34922	154	16425	162	36284	117	40979	95
Acenaphthene	34574	163	21906	114	53332	95	33762	46
Fluorene	64597	335	48300	323	65698	248	54219	324
Phenanthrene	147670	11876	75958	9180	102103	8572	75822	5694
Anthracene	9506	1374	4698	1128	6717	1011	9531	613
Fluoranthene	1735	4467	1950	4988	2281	4481	5203	2984
Pyrene	1591	8429	2567	12128	4212	12127	8128	6239
Benzo(a)anthracene	5	365	0	487	0	456	2	545
Chrysene	7	1243	8	1307	6	1263	7	1513
Benzo(b)fluoranthene	0	77	0	117	0	103	0	233
Benzo(k)fluoranthene	0	105	0	117	0	119	0	174
Benzo(a)pyrene	0	39	0	94	0	81	0	151
Indeno(1,2,3-cd)pyrene	0	10	0	11	0	10	0	27
Dibenzo(a,h)anthracene	0	4	0	6	0	6	0	12
1-Nitropyrene	0	276	0	105	2	118	0	103

12.5-LITER ENGINE RESULTS

Power output of the 12.5-l engine was consistent with the manufacturer's ratings when operating on straight diesel fuel, but problems were experienced when first operating with ethanol-blended fuel. After a period of operation on ethanol-blended fuel, the power output would drop-off and become erratic. It was determined that the performance problems were caused by the ethanol-blended fuel boiling while in the fuel system. The fuel is routed through the head on this engine design, as is common practice with unit injection. In addition, a portion of the unused fuel is re-circulated through the head, rather than being returned to the fuel tank. It is likely that the fuel became too hot and began to boil while passing through the head. To remedy the situation, a small cooler was installed to reduce the fuel temperature prior to reaching the injectors. After this modification was installed, the engine performed well, and testing proceeded.

A summary of averaged, composite values for the duplicate, 8-mode tests of the 12.5-L engine operating on each fuel are presented in Table 12 and Figure 5. Emissions of NO$_x$, particulate, and CO were reduced with the ethanol blended fuels. HC emissions increased with ethanol content.

Smoke test results are presented in Figure 6. Smoke opacity was reduced with increasing ethanol content in all cases. Results are shown for the 7.7 percent blend without the fuel temperature control discussed above. Results are shown for the 10 percent blend with and without temperature control, and with temperature control for the 15 percent blend.

Soluble organic fraction of particulate matter is summarized in Table 13. SOF showed consistent increases with ethanol content in modes 2 and 4. SOF was highest in mode 8. In mode 8, there was little difference in SOF for the four fuels.

Individual hydrocarbon emissions results are summarized in Table 14. As expected, emissions of acetaldehyde and ethanol increased with increasing ethanol content. Other aldehydes tended to increase as well. Benzene and 1,3-butadiene increased with increasing ethanol content, but were all lower than base fuel.

PAH and NPAH results are presented in Table 15. For the lighter molecular weight compounds in the vapor phase, an increasing trend for pyrene is observed, and naphthalene, acenaphthene, fluoranthene are higher in the ethanol blends. Acenaphthylene and acenaphthene are lower in the ethanol blends. For the heavier molecular weight compounds for the vapor phase, benzo(a)anthracene and chrysene show a definite increasing trend with ethanol concentration. Benzo(a)pyrene was higher in the ethanol blends. However, 1-nitropyrene was lower in the ethanol blends. In the particulate-phase decreasing trends for acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene are seen with increasing ethanol content. The heavier compounds are higher for the ethanol blends in the particulate phase, but 1-nitropyrene is lower.

TABLE 12. REGULATED EMISSIONS SUMMARY FOR 12.5-LITER ENGINE AVERAGED, COMPOSITE RESULTS

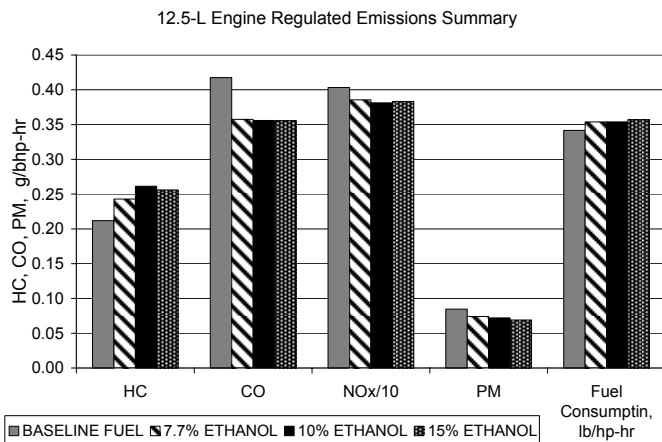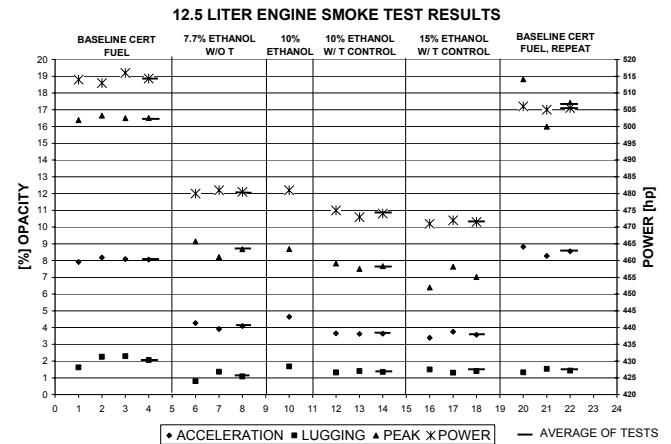| FUEL TYPE	BASELINE FUEL	7.7% ETHANOL	10% ETHANOL	15% ETHANOL	BASELINE FUEL
HC, g/bhp-hr	0.215	0.245	0.260	0.255	0.210
CO, g/bhp-hr	0.420	0.355	0.355	0.360	0.430
NO_X, g/bhp-hr	4.03	3.86	3.81	3.83	4.03
Particulate, g/bhp-hr	0.085	0.074	0.072	0.069	0.091
CO2, g/bhp-hr	491	495	494	492	495
C-B FC, lb/bhp-hr	0.34	0.35	0.35	0.36	0.34
OBS. F-C, lb/bhp-hr	0.34	0.34	0.34	0.35	0.33

Figure 5. Regulated Emissions Summary, 12.5-L Engine

Figure 6. Smoke Test Results For 12.5-L Engine

TABLE 13. SOLUBLE ORGANIC FRACTION BY MODE FOR 12.5-L ENGINE, PERCENT OF TOTAL PARTICULATE MATTER

Fuel Type	BASELINE FUEL		7.7% ETHANOL		10% ETHANOL		15% ETHANOL	
Replicate	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
Mode 1	63.2	51.8	54.8	63.2	65.7	52.0	65.3	65.8
Mode 2	49.1	41.1	59.7	49.1	55.6	58.7	67.5	61.4
Mode 3	40.9	36.9	44.9	40.9	40.7	44.6	44.9	37.9
Mode 4	44.4	32.0	44.6	44.4	42.0	42.2	49.7	47.8
Mode 5	74.6	68.0	67.7	74.6	65.6	68.8	85.4	62.0
Mode 6	80.1	58.0	82.2	80.1	70.3	73.5	100	69.2
Mode 7	63.2	65.7	72.4	63.2	69.0	56.7	56.4	62.4
Mode 8	100	100	100	100	100	100	100	98.0

TABLE 14. UNREGULATED EMISSIONS SUMMARY FOR 12.5-LITER ENGINE AVERAGED, COMPOSITE RESULTS OVER 8-MODE TEST, mg/hp-hr

FUEL TYPE	BASELINE FUEL	7.7% ETHANOL	10% ETHANOL	15% ETHANOL
FORMALDEHYDE	9.16	10.50	11.04	11.78
ACETALDEHYDE	2.78	4.60	5.23	6.65
ACROLEIN	1.05	1.23	0.97	1.25
PROPIONALDEHYDE	0.93	0.95	1.42	1.11
METHYL ETHYL KETONE	0.12	0.15	0.13	0.12
ETHANOL	0.36	17.11	25.12	34.51
1,3-BUTADIENE	1.16	0.21	0.56	0.74
METHANE	1.64	1.66	1.47	1.01
BENZENE	1.13	0.57	1.01	0.98
TOLUENE	1.09	1.20	1.65	1.60
ETHYLBENZENE	0.43	0.47	0.70	0.57
m-& p-XYLENE	0.89	0.74	1.12	0.73
o-XYLENE	0.42	0.39	0.49	0.34
HEXANE	0.03	0.20	0.27	0.15
STYRENE	0.11	0.11	0.09	0.08

TABLE 15. PAH & NPAH COMPOUNDS FOR 12.5-L ENGINE, COMPOSITE RESULTS of 8-MODE TEST, ng/hp-hr

FUEL TYPE	BASELINE FUEL		7.7 % ETHANBOL		10 % ETHANOL		15 % ETHANOL	
COMPOUND/PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE	VAPOR PHASE	PM PHASE
Naphthalene	143664	177	190188	149	154824	98	707495	106
Acenaphthylene	28398	91	22296	64	23297	56	24732	35
Acenaphthene	30382	67	32291	41	31932	25	42270	25
Fluorene	70822	269	56947	184	74026	151	78878	105
Phenanthrene	129464	5001	107998	3246	124868	2566	148862	2054
Anthracene	11327	549	9195	332	10309	275	11839	204
Fluoranthene	2583	1940	3162	1405	3225	1113	4398	1021
Pyrene	4573	4278	7756	4023	8929	3214	11400	2775
Benzo(a)anthracene	18	238	27	368	31	368	66	311
Chrysene	33	601	56	745	76	713	128	668
Benzo(b)fluoranthene	6	71	5	130	8	122	8	142
Benzo(k)fluoranthene	7	73	4	126	5	130	7	115
Benzo(a)pyrene	0	51	0	93	2	118	4	75
Indeno(1,2,3-cd)pyrene	3	13	0	33	3	40	3	35
Dibenzo(a,h)anthracene	0	5	0	6	0	7	0	7
1-Nitropyrene	6	28	1	18	1	18	1	23

DISCUSSION

Evaluation of ethanol blended fuels in engines with three different fuel injection system designs has yielded the following results. Smoke and particulate matter emissions decreased with increasing ethanol content for all engines and as expected, emissions of acetaldehyde were higher for all engines with increasing ethanol content. The ethanol blended fuels yielded improvements in NOx emissions on the 6.8-L (rotary pump line injector) and 12.5-L (electronic unit injector) engines, but were higher for the 8.1-L engine (high pressure common rail injector. CO emissions, however, were increased for the 6.8-L and decreased for the other two. Emissions of benzene and 1,3-butadiene were reduced with the ethanol fuels. No clear trends were discernable for the PAH compounds, but 1-nitropyrene was consistently reduced with use of the ethanol blends. Clearly there is potential for further development work.

SUMMARY AND CONCLUSIONS

This project has generated information on the exhaust emissions effects of various blends of ethanol in diesel fuel. Three concentrations of ethanol in diesel were evaluated on three engines of differing technology and displacement. Three suppliers provided additives for improvement of the characteristics and stability of ethanol blended in diesel fuel. Batches of fuel were prepared at each ethanol concentration with all three additives,

resulting in a 10-fuel matrix (including reference diesel fuel). The nine alcohol-blended fuels were distributed among the three test engines in a way that each engine experienced operation with each additive and each ethanol concentration.

The engines were operated in duplicate over the 8-mode test procedure described in 40 CFR Part 89, and over the FTP smoke test. Regulated emissions were reported in brake specific output (mass per unit work). Unregulated emissions, including soluble organic fraction of particulate (SOF), individual hydrocarbons, ethanol, and aldehydes, polynuclear aromatic hydrocarbons (PAH) and 1-nitropyrene were reported. All engines with all additive suppliers with all ethanol blends met Tier II regulated emissions requirements.

As expected, increasing ethanol concentration led to higher emissions of acetaldehyde (increases ranging from 27 to 139 percent) and ethanol (from trace levels to levels as high as 52 mg/hp-hr). Smoke and particulate matter emissions decreased with increasing ethanol concentration. PM emissions decreased from 13 to 30 percent. Except on the 6.8-L engine, carbon monoxide emissions also decreased, by up to 15 percent, with increasing ethanol concentration. For the 6.8-L engine, CO increased by as much as 22.6 percent. NO_x emissions were reduced with ethanol use on the 6.8-L and 12.5-L engines, with reductions ranging from 5 to 9 percent. Emissions of NO_x increased by as much as 2 percent on the 8.1-L engine.

Emissions of toxics such as benzene and 1,3-butadiene were reduced with the use of ethanol. Benzene emissions were reduced by up to 50 percent with the ethanol blended fuels. Emissions of 1,3-butadiene were also substantially decreased, ranging from 24 to 82 percent reduction.

Isolated trends were noted for certain PAH compounds. There was a decrease in 1-nitropyrene with use of ethanol in all cases. Particulate phase 1-nitropyrene was reduced from 18 to 62 percent. There was also a general increase in heavy PAH compounds in the particulate phase with ethanol use, and although less pronounced, a general decrease in light PAH compounds in the particulate phase with ethanol use.

ACKNOWLEDGEMENTS

REFERENCES

1. Peckham, J., "Ethanol-Diesel Raises Saftey, Performance, Health Concerns," Diesel Fuel News, Vol 5, No. 23, pp 9-11, Chemical Week Associates, 2001.

2. Jackson, M. M.. Corkwell, K.C., and DeGroote, C. C., "Study of Diesel and Ethanol Blends Stability," SAE 2003-01-3191, The Society of Automotive Engineers, Warrendale, PA, 2003.

3. Renewable Fuels Association, "Energy Security." http://www.ethanolrfa.org/factfic_ensec.html

4. Corkwell, K.C., and Jackson, M. M., "Lubricity and Injector Pump Wear Issues with E –Diesel Fuel Blends," SAE 2002-01-2849, Society of Automotive Engineers, Warrendale, PA, 2002.

5. Corkwell, K.C., Jackson, M.M. and Daly, D.T., "Review of Exhaust Emissions of Compression Ignition Engines Operating on E Diesel Fuel Blends," SAE 2003-01-3283, Society of Automotive Engineers, Warrendale, PA, 2003.

6. Walter O. Siegl, Joel F. O. Richert, Trescott E. Jensen, Dennis Schuetzle, Stephen J. Swarin, Jeffrey F. Loo, Arnold Prostak, Don Nagy, Ann M. Schlenker, "Improved Emissions Speciation Methodology for Phase II of the Auto/Oil Air Quality Improvement Research Program--Hydrocarbons and Oxygenates," 930142, Society of Automotive Engineers, Warrendale, PA, 1993

7. Public Law 101-549, "1990 Amendments to the Clean Air Act," November 15, 1990

LIST OF ACRONYMS AND ABBREVIATIONS

ΔP	Delta P – change in pressure
CFR	Code of Federal Regulations, Title 40, Part 89
ASTM	American Society for Testing Materials
bhp	brake horsepower
C-B	Carbon balance
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CVS	Constant Volume Sampler
DEER	Department of Engine and Emissions Research
DNPH	Dinitrophenylhydrazine
FTP	Federal Test Procedure
g	gram or grams
GC-FID	Gas Chromatography-Flame Ionization Detector
HC	Hydrocarbons
hp	Horsepower
hp-hr	Horsepower-hour
HPLC	High Performance Liquid Chromatography
ICGA	Illinois Corn Growers Association
IHC	Individual hydrocarbons
in	Inch or inches
kPa	Kilopascals
kW	Kilowatts
L	Liter
lb-ft	Pound-feet
N-m	Newton-meters
NO_x	Oxides of Nitrogen
NPAH	Nitro Polycyclic Aromatic Hydrocarbons
PAH	Polycyclic Aromatic Hydrocarbons
PUF	Polyurethane foam
PUF/XAD-2	PUF sandwiched with XAD-2 resin
rpm	Revolutions per minute
SOF	Soluble organic fraction

APPENDIX A   FUEL PROPERTIES

ANALYTICAL RESULTS FOR ETHANOL STOCK

Test Parameter	Test Method	Units	Tank 22	Tank 23
API @ 60°F	D4052	none	47.6	47.6
Specific Gravity @ 60°F		none	0.7901	0.7901
Density @ 15°C		grams/L	789.7	789.7
Ethanol content	D5501	weight percent	96.1	95.8
		volume percent	95.6	95.3
Water content	D6304	percent	0.548	0.548

Characterizations of the test fuels are presented in the following table. One should bear in mind that the ASTM methods are not necessarily designed to accommodate a fuel such as an ethanol-diesel blend.   Ethanol is suspended in an emulsion by virtue of the co-solvents and other substances in the various additive packages.

EM-4895-F is the internal designation of the on-highway diesel (nominal 400 ppm sulfur) used in preparing the ethanol blends. The remaining EM- codes are the internal identification codes used in our fuel handling, storage, and inventory system.   Another batch of low-sulfur certification diesel, with essentially the same properties was used in the baseline emissions measurements of the engines, designated EM-4970-F.

TEST FUEL CHARACTERISTICS

Test Parameter	ASTM Test Method	EM-4895-F BaseBlend Stock	EM-4929-F 7.7% EtOH A	EM-4930-F 7.7% EtOH B	EM-4932-F 7.7% EtOH C	EM-4935-F 10% EtOH A	EM-4936-F 10% EtOH B	EM-4937-F 10% EtOH C	EM-4949-F 15% EtOH A	EM-4950-F 15% EtOH B	EM-4951-F 15% EtOH C
Copper Corrosion	D-130	1B	1B	1B	1B	1B	1B	1B	1B	1B	1B
Cloud Point, °C	D-2500	-20	8	8	5	10	12	-6	15	18	-7
Water and Sediment, mL	D-2709	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Viscosity @ 40 °C, cSt	D-445	2.376	2.127	2.110	2.140	2.015	2.093	2.062	1.964	1.962	2.120
Ash Content, mass %	D-482	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Carbon Residue (10% Bottom), mass %	D-524	0.11	0.09	0.14	0.26	0.13	0.15	0.12	0.13	0.18	0.21
Cetane Number	D-613	47.4	48.6	49.9	49.1	46.6	47.5	46.9	47.3	47.6	47.4
Flash Point, °C	D-93	63.3	13.9	10.0	13.9	12.2	10.6	10.6	9.4	11.1	9.4
HFRR, Wear Scar, mm	D-6079	0.525	0.280	0.320	0.410	0.240	0.280	0.405	0.295	0.335	0.410
BOCLE, Scuffing Load, g	D-6078	3800	5350	4350	4200	6500	5750	3550	3850	6050	4400
Density, g/L	D-4052	839.9	835.9	836.8	835.4	835.0	837.0	834.3	833.0	835.2	832.1
Specific Gravity		0.8405	0.8364	0.8373	0.8359	0.8355	0.8375	0.8348	0.8336	0.8358	0.8326
API		36.9	37.7	37.5	37.8	37.9	37.5	38.0	38.3	37.8	38.5
Carbon, mass %	D-5291	86.85	84.29	83.90	84.38	84.23	83.78	83.12	82.67	83.13	81.13
Hydrogen, mass %		13.11	13.08	13.08	12.99	13.26	13.12	13.28	13.13	13.02	12.99
Oxygen, mass % by difference		0.04	2.63	3.02	2.63	2.51	3.10	3.6	4.20	3.85	5.88
Distillation, °C	D-86										
IBP		180.1	73.4	75.1	68.1	60.7	68.8	78.2	65.3	77.3	61.9
5%		195.1	78.6	78.7	76.5	74.7	77.9	79.2	75.6	77.8	78.5
10%		208.5	109.7	154.2	79.8	80.2	79.6	78.1	78.3	78.1	78.7
15%		217.1	197.7	200.9	179.8	80.7	133.3	117.3	81.6	107.2	81.1
20%		224.9	213.3	212.3	205.5	145.7	205.2	202.2	110.1	194.3	167.7
30%		238.6	230.2	229.2	220.7	212.1	223.7	220.9	213.4	219.9	216.7
40%		249.2	243.4	242.5	238.7	233.5	238.1	235.0	232.0	234.4	234.7
50%		258.8	254.5	252.6	250.6	247.2	249.7	247.0	246.6	246.3	249.1
60%		268.0	264.8	263.3	260.8	259.3	260.3	257.3	258.0	257.2	260.3
70%		278.3	275.4	274.6	272.0	270.6	271.3	269.4	269.2	268.7	272.1
80%		290.6	288.4	288.6	285.6	284.3	284.6	282.7	281.7	282.8	285.1
90%		307.7	306.1	307.6	305.4	303.4	302.3	300.8	299.2	303.8	303.9
95%		322.0	322.2	321.4	317.8	320.4	315.2	314.9	310.9	315.7	319.8
FBP		335.9	335.0	326.9	331.7	332.3	334.4	330.2	332.7	324.6	333.4
Recovery, mL		98.2	98	95.6	95	97.5	96.1	96.4	95.4	96.1	97.9
Loss, mL		1.3	1.5	1.2	3.8	1.4	2.9	2.7	3.2	2.9	1
Residue, mL		0.5	0.5	3.2	1.2	1.1	1	0.9	1.4	1	1.1